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*Published in:*  
AIP Conference Proceedings

*Link to article, DOI:*  
[10.1063/1.4922565](https://doi.org/10.1063/1.4922565)

*Publication date:*  
2015

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*  
Marinello, F., Pezzuolo, A., Carmignato, S., Savio, E., De Chiffre, L., Sartori, L., & Cavalli, R. (2015). Elastic-properties measurement at high temperatures through contact resonance atomic force microscopy. *AIP Conference Proceedings*, 1667, [020009]. <https://doi.org/10.1063/1.4922565>

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Citation: [AIP Conference Proceedings](#) **1667**, 020009 (2015); doi: 10.1063/1.4922565

View online: <http://dx.doi.org/10.1063/1.4922565>

View Table of Contents: <http://scitation.aip.org/content/aip/proceeding/aipcp/1667?ver=pdfcov>

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# Elastic-properties measurement at high temperatures through Contact Resonance Atomic Force Microscopy

Francesco Marinello<sup>1, a)</sup>, Andrea Pezzuolo<sup>1</sup>, Simone Carmignato<sup>2</sup>, Enrico Savio<sup>3</sup>  
Leonardo De Chiffre<sup>4</sup>, Luigi Sartori<sup>1</sup>, Raffaele Cavalli<sup>1</sup>

<sup>1</sup> *University of Padova, Department of Land, Environment, Agriculture and Forestry, Viale dell'Università 16, 35020 Legnaro, Padova, Italy*

<sup>2</sup> *University of Padova, Department of Management and Engineering, Stradella San Nicola 3, 36100 Vicenza, Italy*

<sup>3</sup> *University of Padova, Department of Industrial Engineering, Via Venezia 1, 35131 Padova, Italy*

<sup>4</sup> *Technical University of Denmark, Department of Mechanical Engineering, Produktionstorvet 425, 2800 Kgs. Lyngby, Denmark*

<sup>a)</sup> Corresponding author: francesco.marinello@unipd.it

**Abstract.** Miniaturization of products and need for further improvement of machines performance introduce new serious challenges in materials characterization. In particular non-destructive mechanical testing in the sub-micrometer scale is needed to better understand and improve micro-manufacturing operations. To this regard, some open issues are of particular interest: low depth of penetration, high lateral resolution and measurements at elevated temperatures. An interesting solution is given by acoustic microscopy techniques, which can be successfully implemented for advanced research in surface elasticity, allowing fast direct and non-destructive measurement of Young's modulus and related surface parameters.

In this work an instrument set up for Contact Resonance Atomic Force Microscopy is proposed, where the sample with is coupled to a heating stage and a piezoelectric transducer directly vibrate the cantilever during scanning, in order to allow exploitation of high resolution measurements at relatively high temperatures. Such instrument set up was undergone a set of calibration experiments in order to allow not only qualitative but also quantitative characterization of surfaces. The work was completed with a feasibility study with mechanical and topography measurements at temperatures as high as 150°C, with lateral resolution lower than 100 nm.

**Keywords:** Young's modulus, elasticity, polymer blend, microscopy

**PACS:** 07.79.-v, 43.35.Sx, 62.20.-x

## 1. INTRODUCTION

Recent trend in miniaturization in many fields of science and technology introduces new challenges in materials characterization, with an increasing need for fast non-destructive characterizations with sub-micrometer resolution. In particular, a great interest is being shown in micro- and nano-mechanical testing [1-5]. For the purpose, some techniques have been developed and successfully applied in several technological fields, mainly related to precision- and micro-manufacturing, surface coating and new materials development.

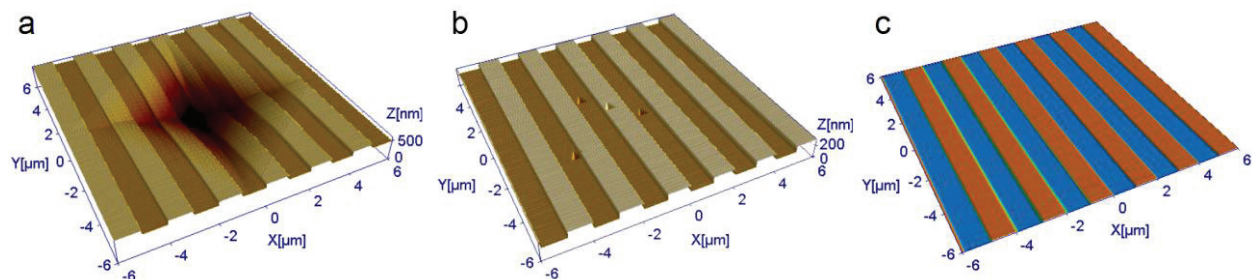
Instrumented nanoindentation is certainly the most widely used technique for determining local mechanical properties of materials ranging from metals and ceramics to polymeric and biological materials. Such technique is based on the loading of a tip over a surface, with application of a specified force or a given displacement. Measured forces and displacements over a complete loading cycle then give information on local surface properties, such as elastic modulus ( $E$ ) and hardness ( $H$ ). Main limitations for this technique arise from finite tip dimensions and loads. Indeed, surface material response is influenced by substrate response for a depth of approximately 5-10 times the

indented depth, while laterally indentations can be taken at a minimum distance of at least two times the indentation width. As a consequence, lateral resolution for nanoindentation is limited to about 100-300 nm, while films not thinner than 50-100 nm can be characterized (Figure 1a and 1b) [6]. Furthermore a single load cycle takes at least some minutes, therefore several hours measurements are needed to obtain dense characterization maps.

A valuable alternative is given by implementation of Scanning Probe Microscopy (SPM) techniques. SPM provides nanoscale characterization of a variety of surface properties, involving geometry, friction, electric and magnetic fields as well as attractive and repulsive forces in proximity of the substrate [4-9]. Contact Resonance Atomic Force Microscopy (CR-AFM) is a recently developed SPM technique used for advanced research in surface elasticity, and includes specific scanning modes, namely Atomic Force Acoustic Microscopy (AFAM) or Ultrasonic Atomic Force Microscopy (UAFM). In fact CR-AFM uses local elasticity to provide relatively fast direct and non-destructive imaging, as well as direct quantitative measurement of Young's modulus and related surface parameters.

Contact Resonance Atomic Force Microscopy is a near-field technique, mainly dominated by interface material properties, and exploiting the spatial resolution typical of SPMs (Figure 1c). For these reasons such technique can potentially overcome the limitations of nanoindentation.

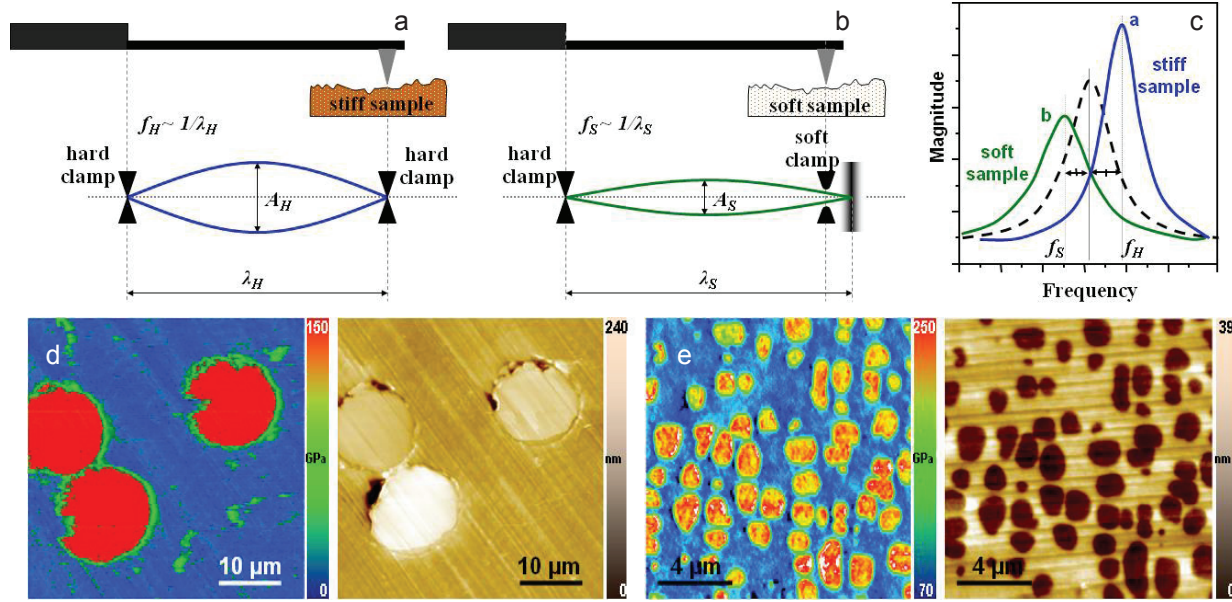
CR-AFM has already demonstrated its good performance in a number of different applications [8-11], nevertheless its quantitative application is still difficult, due to the number of factors influencing measurement output and consequently parameters estimation.



**FIGURE 1.** Effect of micro-indentation (a) and nano-indentation (b) on surface topography. In case of thin films or micro-features, the relatively large dimensions of indenters limit the possibility of quantitative characterization, which are conversely allowed by near-field surface Contact Resonance Atomic Force Microscopy techniques (c).

## 2. ACOUSTIC PRINCIPLE

In Contact Resonance Atomic Force Microscopy techniques the probe or the sample under investigation is vibrated at ultrasonic frequency, while the cantilever is contacting and scanning the sample surface through the tip. Any standard AFM with lateral actuation of the probe (the so called “scan by probe” set up) can be operated for acoustic measurements, simply implementing a longitudinal ultrasonic piezoelectric transducer on the probe or under the sample. A schematic view of acoustic probe microscopy interaction is represented in Figure 2. When not approached to the sample surface, the sample can be regarded as a beam structure fixed only at one end (typically a silicon chip) and with the other end (on the tip side) freely vibrating. Once engaged to the sample, with the tip interacting with the surface, the cantilever changes its boundary conditions, with the free end turned to a coupled end. Consequently to the new constrain, the flexural vibration modes and frequencies change. In particular resonance frequency shifts occur, which are proportional to the new constrain stiffness and then on the effective contact stiffness  $k^*$  occurring between the tip and the sample surface. As shown in Figure 2, one node of the vibration lies at the base of the chip where one end of the cantilever is fixed, while the second node can be localized close to the tip. In the case the probe is in interaction with a hard/stiff surface the node lies in the very proximity of the tip apex (Figure 2a); on the other hand, if the surface is softer, the node can be considered to lie deeper into the sample (Figure 2b). Accordingly, when the probe moves from a stiffer to a softer region, the second node shifts and the wavelength increases ( $\lambda_H < \lambda_S$ ) with an inversely proportional variation in resonance frequency ( $f_H > f_S$ ). Also, being dampening larger in the case of softer regions, the relative peak at the resonance frequency has smaller amplitude.



**FIGURE 2.** Acoustic probe microscopy interaction when the tip is interacting respectively with a stiff (a) and a soft (b) surface, generating different flexural vibration wavelengths and frequencies (c) [12]. Below: examples of acoustic measurements with corresponding topography on different surfaces: (d) polypropylene with glass fibres, (e) inconel 738.

Allowing the AFM electronics to monitor flexural vibration spectra at each point, revealed frequency shifts are interpreted through an analytical model of the cantilever beam dynamics. Typically the simplest and however effective applied model to describe the spring contact stiffness  $k^*$  between the tip and the sample is a purely elastic interaction. From the values of contact stiffness  $k^*$ , typically taking advantage of a Hertzian contact mechanics model, the elastic properties of the sample can be calculated, in terms of reduced Young's modulus ( $E^*$ ) and indentation modulus ( $M_t$ ). Some examples of acoustic measurements are reported in Figure 2d-e. Simultaneously with acoustic imaging (which can be properly converted to quantitative mapping of mechanical properties) acoustic techniques provides also reconstruction of surface topography. In this way different mechanical properties can be directly associated to different surface topography structures.

### 3. CR-AFM INSTRUMENT

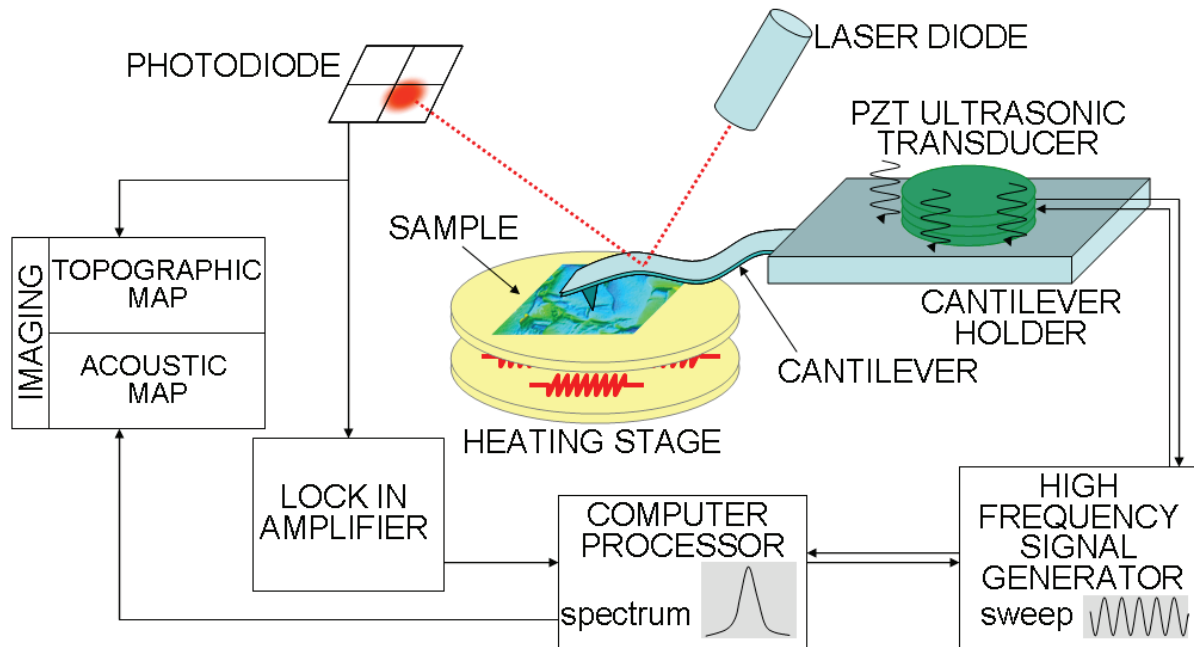
In the typical CR-AFM set up, commonly implemented for mechanical characterizations, a transducer vibrates the sample under investigation, in an Atomic Force Acoustic Microscope configuration. In the present work an existing AFAM set up has been modified in order to allow high temperature measurements, moving the position of the piezoelectric ultrasonic transducer from the sample to the probe in a UAFM configuration. A sinusoidal excitation is then given by a frequency generator to the piezoelectric transducer which is coupled to the probe through the chip which holds the cantilever. With such instrument set up any stage can be placed beneath the sample, as for instance for increasing the maximum measurable range [13] or for *in situ* tensile tests [14]. Specifically a heating device can be placed, or alternatively a stage exploiting any given function, as for instance providing a tension, a strength or a magnetic field to the sample. A simplified block diagram of the experimental apparatus is reported in Figure 3.

The sample, mounted on a heating stage, is contacted by a probe which at its basis (on the chip, where the cantilever is fixed) is clipped to an ultrasonic contact transducer, with a piezoelectric element.

The probe can be excited by the transducer which emits a continuous longitudinal sinus wave, with frequencies between 10 kHz and 1 MHz. These longitudinal waves propagate through the cantilever and the tip getting to the surface in the proximity of the very end of the tip. The flexural mode of cantilever depends on the stiffness at the contact between the tip and the sample and is monitored by a beam bounce feedback. Amplitude and phase of the resulting cantilever vibration are detected through an optical lever system, consisting of a laser diode and a segmented photodiode. The laser deflected by the cantilever backside is sensed by the photodiode and decomposed:

- the deflection part is directly used to generate the topographic map;
- the amplitude of the vibration is amplified and detected through a lock-in amplifier.





**FIGURE 3.** Set-up for CR-AFM imaging. An ultrasonic piezoelectric transducer is coupled to the sample and excites cantilever holder vibrations which are then transferred into the cantilever. The laser from a diode is reflected by the cantilever and focused through a lens and a mirror to a segmented photodiode: collected signal is then processed by a fast lock-in-amplifier to provide amplitudes or phases of the resulting cantilever vibration.

Then a spectrum of the cantilever response versus generated frequency can be produced by sweeping the transducer excitation frequency and monitoring the lock-in output. In this way, at each probe position, the relative height and a spectrum are generated. Point by point, the relative maximum of the spectrum can be found: such information is then used to control the transducer resonance frequency by the processor, and to generate the acoustic map, which -opportunistically processed- can be converted into either contact stiffness, or reduced Young's modulus, or indentation modulus maps.

## 4. EXPERIMENTAL STUDY

### 4.1 Modified layout analysis

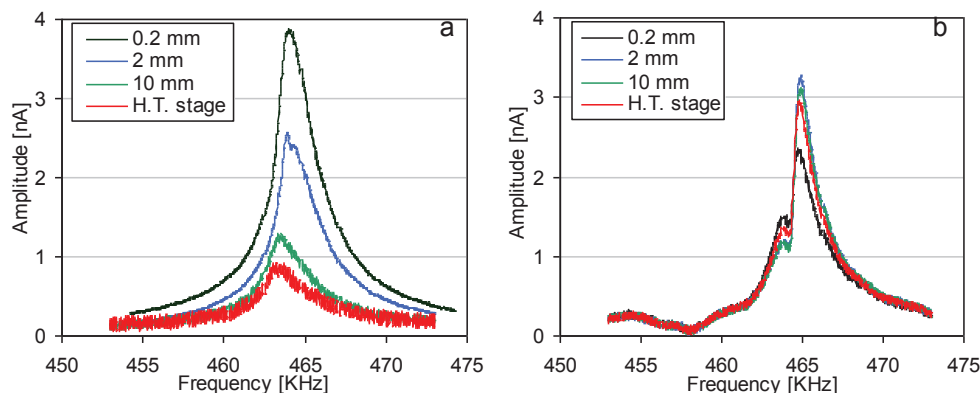
The merit of the modified design is that the sample can be freely positioned on any kind of stage, and in particular on a heating stage. This is not possible in the traditional CR-AFM layout, where the sample is directly positioned over the ultrasonic transducer. Indeed in such layout not only there is no room for directly accessing the sample interface (which is completely attached to the transducer) but also a temperature variation due to the presence of a heating stage could cause depolarization of the piezoelectric transducer. Indeed whenever the ceramic element is heated above the Curie point (which typically ranges between 180°C and 400°C), piezoelectric properties are lost: in practice, the operating temperature must be substantially below the Curie point, so that experiments are usually limited to ambient temperature.

The modified CR-AFM layout has the advantage to overcome such limitations, but on the other hand tends to take a sharp toll on the spectrum signal [15]. As part of the present work, experimental studies were carried out in order to study how the sensed signal changes when modifying the instrument set up. By way of example Figure 4 shows spectra taken with the same instrument and the same probe contacting the same sample position: specifically the probe had a free resonance frequency of 87 kHz, with a force constant of about 2 N/m, contacting a glass slide surface. In the first case (Figure 4a) the ultrasonic excitation was sent via the sample as in previous set up while in the second case (Figure 4b) was sent to the chip as in the modified CR-AFM set up. Revealed spectra clearly show how, particularly in the case of thin samples (0.2 mm thick), in the previous set up the optimized signal is very clear, with a well defined and recognisable resonance peak and a low signal to noise rate (Figure 4a). The quality sensibly

reduces as the thickness of the sample increases or when a heating device (turned off) is inserted in between the sample and the transducer (see red curve in Figure 4a).

On the other hand, revealed spectra with excitation from the probe are certainly worse than in the case of the directly excited 0.2 mm thick sample (Figure 4b). Indeed in the modified CR-AFM set up the optimization of resonance parameters brings to relatively higher signal to noise rates and to double peaks, not present in the optimized previous set up. The presence of a spurious peak in the close proximity of the resonance peak has been encountered during different experiments in the modified set up. This has been associated to a secondary noise phenomenon related to the resonance of the chip (normally modelled as an infinitely stiff constrain) supporting the cantilever. In order to avoid the spurious peak to influence the detection of the resonance flexural frequency, a larger frequency range was considered in the procedure for acoustic analysis, combined with a more robust filter to allow the software not to converge to the wrong local minimum.

If by one side the modified set up present a worse signal, on the other hand its performance is almost independent from the sample thickness or from the presence of a heating stage under the sample, and variations are mainly due to the repeatability of the instrument or from external noise affecting the signal sensing. In other words the modified set up can be preferred when experiment modification asks for a non optimized set up, with thick samples or with functional stage to modify the sample state.



**FIGURE 4.** Spectra as revealed by the photodiode (units are in nanoAmpere) and enhanced by the lock-in amplifier, for the previous (a) and the new CR-AFM (b) set up, in the case of samples having different thicknesses (0.2, 2 and 10 mm) and in the case of the presence of a high temperature stage.

## 4.2 Experimental analyses

A set of experiments was run to verify the applicability of the technique for relatively high temperature mechanical characterizations. Experiments were preceded by a calibration session in order to allow exploitation of quantitative measurements. To this end two main steps are needed: monitoring of tip shape and actual calibration<sup>16</sup>.

Polymers soft interface typically has only a minor effect on tip wear. However AFM tip shape characterization was considered before and after each CR-AFM test, highlighting overall constancy of tip radius ( $r=24 \pm 5$  nm). Some contaminations (presumably polymer residuals) were evidenced on tip flank, after high temperature measurements, however it is worth noting that tip flank has only a negligible effect on overall resonance frequency.

Calibration of resonance frequency was made comparing resonance frequencies with Young modulus estimated through nanoindentation tests on reference surfaces as detailed in previous work [16].

For high temperature experiments, a poly-methyl-methacrylate and styrene-butadiene-styrene (50% PMMA - 50% SBS) blend was used [17]. The blend was produced in a toluene solution, kept at 110°C for a few minutes. Thin films deposition (as thick as a few microns) was achieved by spin-coating deposition (2000 rpm, for 30 seconds) on a silicon substrate.

Once deposited, PMMA forms a netlike structure, filled with the SBS phase: SBS agglomerates into spheroidal domains, with an average diameter ranging between 0.2 and 1.5  $\mu\text{m}$ . Mechanical characterization of such kind of structure is actually not possible with instrumented nanoindentation, due to the small size of the phases, and to the reduced film thickness.

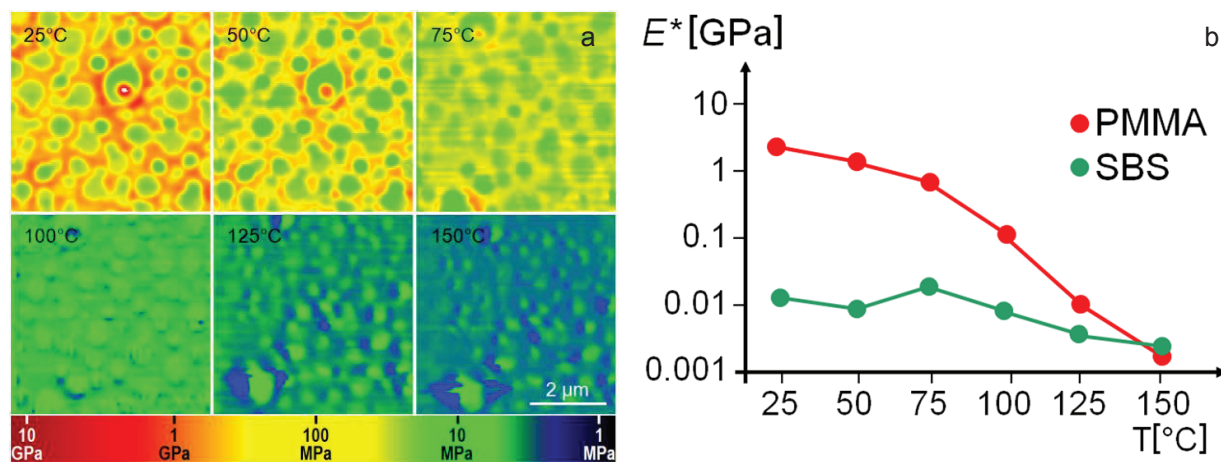
Atomic force acoustic measurements in the modified set up were carried out with the sample positioned on a resistive heating stage, capable of a maximum 200°C temperature. Temperature was varied from 25°C up to 150°C,

with a rate of about 5°C/min. At 25°C steps, temperature was stabilized for one minute and then an acoustic and a topographic measurement were taken, on a 5×5 μm range with a 64×64 points sampling (corresponding to about 80 nm lateral resolution). Each measurement took about 6 minutes (meaning 0.05 seconds per point), and the whole experiment about one hour. Reduced Young's modulus  $E^*$  maps directly achieved from the acoustic measurements are reported in Figure 5a. After segmentation, average  $E^*$  values were separately estimated for PMMA and for SBS in each map: values are graphically reported as a function of temperature in Figure 5b. The experiment with the modified design AFAM characterization demonstrates the different behaviour of SBS (the green phase) and PMMA (the surrounding matrix) at increasing temperatures. In particular it is clear how PMMA elastic modulus diminishes with a rapid variation at about 100°C, while SBS properties stay almost constant during temperature evolution.

PMMA and SBS phases mapped in Figure 5 are well defined at low temperatures, while images are visibly blurred and polymer phases not well separated at high temperatures. Such blurring increases the difficulty in data processing and in particular in image segmentation: this is most probably the cause of the positive deviation and higher value estimation of SBS Reduced Young's modulus at 75°C (Figure 5b).

Additionally at highest temperatures (125°C and above), topographies exhibits distortions (on the bottom left of images) most probably due to some stitching phenomena of the melt polymer phase to the tip.

At relatively high temperatures (75°C and above) horizontal stripes are visible: they are typical of SPM raster scanning and are due to nanometric average distance variations between the probe and the surface, when moving from one scanned profile to the subsequent one. Such distortions are typically associated to thermal drift phenomena and can be only partially limited, by increasing thermal insulation and instrument stabilization [18].



**FIGURE 5.** (a) Reduced Young's modulus maps of a PMMA-SBS blend, at increasing temperatures, from 25°C up to 150°C. Scan range 5×5 μm, lateral resolution 80 nm. (b) Average reduced Young's modulus  $E^*$  for PMMA and for SBS as a function of temperature.

The mechanical characterization and related quantitative results (Figure 5) are extremely interesting: indeed for the first time AFAM mechanical measurements have been produced reporting simultaneously all the following advantages.

- Relatively high temperatures of measurement: with currently available equipment using the modified instrument set up, measurements can be done up to 300°C without the risk of depolarizing the ultrasonic transducer connected to the probe, which is not possible with standard CR-AFM technique with AFAM configuration.
- Relatively short measurement time: each map, containing more than 4000 points was taken in about 6 minutes; the same time is needed by other instrumented nanoindentation to take a measurement on one or two points.
- High resolution: a lateral resolution of a few tens of nanometers is not achievable with any other instrument.
- Measurement of thin sample thickness: CR-AFM is only minimally sensitive to substrate effect and measurements can be performed on samples as thin as a few tens of nanometers; this is actually not possible with the standard instrumented nanoindentation.

Some problems related to the technique are still under investigation, and are mainly dealing with the influence of the tip shape. The control of the tip size and radius of curvature stability has still to be improved. In particular experiments are running to understand the effect of contaminations on the tip surface, particularly relevant when measurements are carried on sticky surfaces, as in the case of polymers at relatively high temperatures [16].



## CONCLUSION

In the present work an instrument set up modification is proposed for Contact Resonance Atomic Force Microscopy (CR-AFM), where a piezoelectric transducer has been positioned to directly vibrate the cantilever during scanning. With such design, the excitation is moved from the sample to the scanning probe, so that the sample (no matter its thickness) can be freely coupled with any kind of stage, and specifically to a heating stage. In the modified configuration both the excitation and the signal collection are localized within the probe; therefore, advanced signal amplification and filtering are needed to separate probe vibration spectrum and locally identify resonance frequency.

The implemented instrument set up was undergone a first study. In particular mechanical characterizations combined with traditional topography characterization at temperatures as high as 150°C, with a lateral resolution better than 100 nm, were carried out on a PMMA-SBS blend, allowing for simultaneous characterization of both phases at different temperatures.

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